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PATENT SPECIFICATION



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428,445

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(Under Section 91, Sub-sections (2) and (4) (a) of the Patents and Designs Acts, 1907 to 1932, a single Complete Specification was left in respect of this Application and of Application No. 22090/33 (428,361), and was laid open to inspection on Feb. 12, 1934.)

COMPLETE SPECIFICATION**Improvements in methods of preparing Fluorine Derivatives of Hydrocarbons**

We, KINETIC CHEMICALS, INC., a corporation organized and existing under the laws of the State of Delaware, United States of America, located at Du Pont 5 Building, Wilmington, State of Delaware, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to methods of fluorinating acyclic hydrocarbons, or aryl derivatives thereof. 15 In Specification No. 291,168 the fluorination is effected in the presence of a catalyst which consists of a halide of a metal whose halide has the property of mutually exchanging its halogen with hydrogen fluoride, and whose fluoride has the property of mutually exchanging halogen with the halogen derivatives of the hydrocarbon whose fluoride it is desired to obtain. Antimony halides, 25 particularly antimony fluorochlorides, are disclosed as suitable catalysts. The catalyst is desirably maintained in the liquid state.

Liquid catalysts are subject to considerable loss by volatilization necessitating recovery apparatus, while they tend to increase the hazards involved in working the process particularly when they are toxic in character.

According to this invention the improved method of fluorinating acyclic hydrocarbons, or aryl derivatives thereof, comprises reacting a hydrocarbon halide, containing halogen other than 40 fluorine, and hydrofluoric acid in the presence of a catalyst consisting of carbon.

Suitable apparatus for effecting the reaction may consist of vaporisers for 45 vaporising the hydrogen fluoride and acyclic hydrocarbon halide, a heated reaction chamber containing the catalyst through which the vaporised reagents are simultaneously passed, scrubbers containing alkali for removing excess acid from

the reaction vapours, and scrubbers containing strong sulphuric acid or other suitable dehydrating agent for drying the gases, and finally liquefying and storing devices. Traps, gauges, valves and additional inlets etc. may be disposed at convenient places in the system as will readily occur to one skilled in the art. Those portions of the apparatus which come into contact with the hydrogen halide during the reaction are usually made of or lined with some corrosion resistant material. Copper or monel metal are suitable. The hydrogen halide removing scrubbers may however sometimes with advantage be constructed of phenol-formaldehyde resins or of lead. For those parts of the apparatus following the removal of the corroding materials, ordinary construction materials may be used; cast iron, wrought iron, steel etc.

In regard to this we may remark that we are aware of Specification No. 259,997 which discloses the use of sheet metal and monel metal for the reaction chamber and fractionating column of an apparatus for use in the manufacture of fluorine-containing derivatives of hydrocarbons in which the fluorine for replacing the halogen atoms in an aliphatic hydrocarbon halide is obtained from antimony trifluoride in the presence of antimony pentachloride acting as a catalyst.

The carbon may be of any origin; charcoal obtained by destructive distillation of carbonaceous material is suitable. The carbon should preferably be absorptive, while activated and acid washed carbons give particularly good results. It is in general desirable that the physical form of the catalyst be such that it does not tend to form dust and pass out of the catalyst chamber with the gas stream.

While the reaction is preferably effected in the vapour phase, the temperature and pressure may be so adjusted that at least one of the reagents

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is in liquid phase when in contact with the catalyst. HF is a liquid at 80° C. under a pressure of about 5-6 atmospheres.

5 The temperature at which the reaction may be effected varies over a wide range, depending upon the material to be fluorinated and the nature of the catalyst.

10 Superatmospheric pressures are advantageously used especially in fluorinating compounds which split off a halogen acid at high temperature; high pressure also allows a greater capacity per unit volume

15 of catalyst.

It will be recognized that the invention is applicable to the fluorination of a large number of halogen-containing carbon compounds. As specific examples of such compounds may be mentioned methylene chloride (CH_2Cl_2), fluoro-trichloromethane (CFC_3), ethyl chloride ($\text{CH}_3\text{CH}_2\text{Cl}$), isopropyl bromide ($\text{CH}_3\text{CHBrCH}_3$), ethylene dibromide

25 ($\text{CH}_2\text{Br}-\text{CH}_2\text{Br}$), tetrachloro-ethane ($\text{CHCl}_3-\text{CHCl}_2$), trichlor-ethylene ($\text{CHCl}=\text{CCl}_2$), chloroform (CHCl_3), carbon tetrachloride (CCl_4), trifluoro-trichloro-ethane ($\text{C}_2\text{F}_3\text{Cl}_2$), symmetrical di-

chloro-ethane ($\text{CH}_2\text{ClCH}_2\text{Cl}$), hexachloroethane (C_6Cl_6), tetrachlor-ethylene ($\text{Cl}_2\text{C}=\text{CCl}_2$) and halogen derivatives of higher members of the aliphatic series.

35 As further examples of compounds containing an acyclic carbon atom having attached thereto a halogen other than fluorine may be mentioned benzo-trichloride ($\text{C}_6\text{H}_5\text{CCl}_3$), benzo-difluorochloride ($\text{C}_6\text{H}_5\text{CF}_2\text{Cl}$), benzo-fluoro-dichloride ($\text{C}_6\text{H}_5\text{CFCl}_2$) and ring-substituted

40 benzo-trichlorides containing halogens (e.g. chlorine and bromine). In fluorinating benzo-trichloride derivatives containing chlorine atoms in the aryl portion thereof, it has been noted that the chlorine atoms in the acyclic portion may be replaced by fluorine without affecting the chlorine atoms in the aryl portion.

Where the original acyclic halogen derivative contains hydrogen, a substitution of halogen for hydrogen may occur during the fluorination operation if a free halogen such as chlorine is present during the fluorination reaction.

55 Examples of such reactions are those taking place when methylene chloride or tetrachloro-ethane are fluorinated.

When the original acyclic halogen derivative is unsaturated, the addition of 60 halogen and the introduction of fluorine may take place in the same operation. For instance, fluoro-chloro derivatives of ethane may be prepared by passing tetra-chlor-ethylene or trichlor-ethylene, 65 hydrogen fluoride and chlorine through

the catalyst under suitable conditions of temperature and pressure.

The hydrogen fluoride may contain impurities such as water.

In the following Examples the parts are by weight.

EXAMPLE 1.

Gaseous HF is passed through liquid CCl_4 heated to about 70° C.; the resulting vaporous mixture is passed through 75 a column of granular charcoal maintained at about 400° C. At a rate of about 30 parts HF per hour, 86% utilization of the HF is effected.

The gases from the reaction chamber are washed with water, caustic alkali and sulphuric acid respectively. The alkali and acid scrubbers are maintained at between 50° and 60° C.; the product is condensed at -40° C. to -50° C. and recovered in liquid form. On fractional distillation it yields 80% difluorodichloro-methane, 50% fluorotrichloromethane and 10% carbon tetrachloride.

EXAMPLE 2.

At the rate of 26 parts per hour HF is passed through boiling CHCl_3 , and the resulting vaporous mixture through a 20" x .75" column of charcoal, the temperature of which is gradually raised from 50°-300° C. The reaction starts at about 200° C. 85% of the HF is used up. The gaseous products are washed in aqueous NaOH and concentrated sulphuric acid. They are condensed at -20° to -30° C. and the condensate fractionally distilled to yield 10% difluoro-chloromethane, 60% fluorodichloromethane and 30% chloroform.

EXAMPLE 3.

Hydrogen fluoride vapour was passed through trifluoro-trichloro-ethane, heated to a temperature of about 20°-25° C. and the mixture of vapours was then passed through a column of small pieces 110 of carbon maintained at a temperature of about 500°-600° C. The reaction product was washed free from acid, dried, condensed and subsequently fractionally distilled. Under the conditions 115 of reaction approximately 50% of the hydrogen fluoride was utilized with a passage of about 40 parts of hydrogen fluoride per hour. The products isolated by fractional distillation were penta-

120 fluoro-chloro-ethane ($\text{C}_2\text{F}_5\text{Cl}$) and tetra-fluoro-dichloro-ethane ($\text{C}_2\text{F}_4\text{Cl}_2$). The pentafluoro-chloro-ethane which is apparently a new product never before isolated boils at about -40° C. at atmospheric pressure. The tetra-fluoro-dichloro-ethane boils at about +4° C. at atmospheric pressure.

EXAMPLE 4.

20 parts dry HF and 150 parts CCl_4 .

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are vaporised per hour, mixed and passed through a column of 260 parts commercial granular active carbon (density about 0.5) maintained at about 400° C. 5 held in a metal tubular chamber having a length about 50 times its diameter. The catalyst is heated by electrical means. The gas mixture evolved consists of HCl, CCl_4F_2 , CCl_3F , HF and CCl_4 . It is 10 cooled in a preliminary condenser to about 45° C. to separate out most of the CCl_4 . This may be reused. Where CCl_4F_2 is the product desired the condenser is maintained at about -10° C. 15 to separate also most of the CCl_4F_2 , which also may be reused.

The HCl and HF are removed by washing in water and 9-10% NaOH. The gases are dried by passage through 20 90-95% sulphuric acid, and eventually condensed at about -50° C. The product consists chiefly of CCl_4F_2 , with some CCl_3F and CCl_4 ; it is fractionally distilled, preferably under pressure, to 25 yield 85-90% conversion of the HF.

EXAMPLE 5.

Chloroform is substituted for the carbon tetrachloride of Example 4 and the temperature of the catalyst is maintained at 300° C. The preliminary condenser is cooled to 0° C., and the caustic and sulphuric acid scrubbers are held at about -50° C. The condensate consists of CHCl_3F , CHCl_2F_2 , and some CHCl_2 . 30 They are fractionally distilled under superatmospheric pressure to yield 85-90% conversion product based on the HF used.

EXAMPLE 6.

40 Substituting 250 parts trifluorotrichloroethane for the carbon tetrachloride of Example 4 and maintaining the catalyst at 500° C. yields tetrafluoro-dichloroethane and pentafluoro-chloroethane in 45 yields of about 50% conversion of the HF. The preliminary condenser is cooled to 0° C. and the final condenser to -50° to -60° C.; the scrubbers are maintained at 40° C.

EXAMPLE 7.

50 150 parts symmetrical dichloroethane are reacted with 20 parts HF per hour, in the manner set forth in Example 4, the catalyst being maintained at 55 300°-400° C. The partial or preliminary condenser is cooled to 20° C.

A mixture known to contain vinyl chloride and most probably containing fluoro-chloro-ethane, difluoro-ethane and

vinyl fluoride was obtained. The amounts of vinyl compounds increase with operation at higher temperature. 60

The products of the invention find application for various commercial purposes. Thus, difluoro-dichloro-methane, fluoro-dichloro-methane (CHFCl_2) and fluoro-trichloro-methane (CCl_2F) are widely used as refrigerants. The new product penta-fluoro-chloro-ethane, described in Example 3 also possesses very desirable properties for low temperature refrigeration. Some of the higher boiling compounds, such as trifluoro-trichloro-ethane and fluoro-trichloro-methane, are generally applicable for use as solvents or reaction media. Moreover, many of the products investigated have been found to be advantageous in that they are odourless, non-inflammable, non-corrosive and non-toxic. 70

We are aware that it has previously been proposed to manufacture methane derivatives containing chlorine and fluorine by acting with hydrogen fluoride upon carbon tetrachloride vapour in the presence of a mixture of antimony trichloride and antimony penta chloride which might be carried on a porous substance, such as coke. 75

According to the invention the catalyst employed consists of carbon and no addition of metal halides such as have previously been proposed as catalysts for the reaction is made.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:-

1. An improved method of fluorinating acyclic hydrocarbons or aryl derivatives thereof by reacting a hydrocarbon halide, containing halogen other than fluorine, and hydrofluoric acid in the presence of 100 a catalyst consisting of carbon.

2. An improved method as claimed in Claim 1 in which the carbon is activated.

3. The methods of fluorinating acyclic hydrocarbons substantially as set forth in 110 the foregoing Examples.

4. The improved methods of fluorinating acyclic hydrocarbons or aryl derivatives thereof, substantially as hereinbefore described.

Dated this 24th day of April, 1935.
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